Analysis of the effect of composite peat-based hydrophobically-modifying additives on the properties of Portland cement and cement mortar

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SUMMARY

This article examines constraints on the use of peat additives for hydrophobic modification of cement in conjunction with the current technological processes of industrial cement production. The effects of complex hydrophobic modifying additives (HMAs) prepared using different combinations of peat, the organosilicon NGL-94 and oleic acid on the properties of cement and cement mortars are investigated in a series of experiments that emulate industrial processes. The main advantages and disadvantages of the experimental compositions of the modified cement are determined in terms of physical and mechanical properties of the eventual mortar when set. The reduction in strength of the experimental samples is caused by the high air content of the cement paste, which can be linked to short-cuts in modern experimental methods. On the basis of the results, a method is proposed for industrial use of composite HMAs in Portland cement production that incorporates additional ingredients to suppress the entrainment of air into the hardening cement mortar and makes it possible to produce hydrophobically-modified cement that fully meets the requirements of modern standards.

KEY WORDS: air entrainment, composite HMA, defoamer, ethylhydrosiloxane, oleic acid, porosity, sorption

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INTRODUCTION

The method for applying hydrophobic components of peat to dispersed mineral materials is based on the thermal separation of labile bitumen from peat and its subsequent sorption onto the surfaces of the mineral particles (Misnikov 2016). A few publications (Misnikov *et al.* 2016, Misnikov & Korolev 2017) demonstrate the positive effects of hydrophobic modification using peat on the properties of powdered materials and propose potential applications in industrial processes. The main obstacle to developing practical applications for industry is the need to identify products for which it is technologically feasible to combine hydrophobisation using peat with established industrial processes so as to scientifically substantiate and introduce the procedure within the constraints of equipment (e.g. reactors) already in place. For example, during the production of gypsum binder it is possible to combine the thermo-chemical decomposition of peat with the process of firing gypsum dihydrate in the cooking boiler (Misnikov 2018). In this case, the bitumen that forms during thermal separation of peat will settle on the surfaces of the mineral particles after conversion of gypsum dihydrate to gypsum hemihydrate by removal of water.

To apply the method elsewhere, it is necessary to minimise production costs whilst complying with current industrial standards. This becomes obvious in technological substantiation of the possibility of using hydrophobically-modifying additives in the production of Portland cement. The main problem here is the limit imposed by both European and Russian standards (EN 197-1, GOST 31108-2003, GOST 10178-85) on the content of organic additives (0.2–0.5 %) that can be introduced into the mineral binder when grinding the clinker components. This requirement is fulfilled by the method for obtaining a model hydrophobically-modified cement presented by Misnikov (2016). However, in adjusting the method to industrial operating conditions it emerged that the concentration of the hydrophobically-modifying additive (HMA) based on peat must be at least 2 % in order to achieve a stable water-repellent effect (Misnikov 2014). Moreover, in some cases, such a concentration begins to negatively affect the physical and chemical characteristics of the mineral binder.

One possible solution for this problem is to apply composite HMAs, by adding traditional hydrophobic additives to the peat matrix in order to enhance the hydrophobic effect (Khigerovich & Baier 1979, Pashchenko 1987, Barnat-Hunek & Smarzewski 2015, Lagazzo *et al.* 2015). The traditional additives include naphthene soap, asidol, oleic acid, organosilicon liquids, "raw" peat bitumen, modified wax and other well-known water repellents. There are

problems with using many of these additives alone, due to the extremely low required concentrations (0.04–0.1 %) and the associated needs for accurate dosing, uniform distribution within the powder, etc.

During the application of hydrophobising additives to cement, as well as to mortar or concrete mixtures, the following effects occur (Khigerovich & Baier 1979):

- significant deterioration of cement wettability with water;

- hydrophobisation of concrete and, as a consequence, a decrease in the rate of capillary suction of moisture, which favourably affects its durability;

- stronger entrainment of air into the system than when using hydrophilising adhesion agents.

One of the operations for obtaining peat-modifying additives is mechanical dispersion of the material. Mechanical dispersion of peat leads, first of all, to the destruction of its native porous structure. In addition, the chemical composition of the material may change as the type and intensity of mechanical action on its organic matter changes. In most cases, peat dispersion involves five types of mechanical action on the material; namely smashing, cutting, crushing, splitting and abrasion (or combinations of these). As a rule, mechanical processing also reduces the size of the coarse-dispersed fraction of the peat without changing (or hardly changing) its chemical properties. At the same time, the application of high-energy mechanical action to organic matter makes it possible to give new properties to the processed product. Mechanical processing methods for peat include grinding in a ball mill or similar grinding unit, where the local temperature in the zone of contact between peat particles and the working body can reach values corresponding to pre-pyrolysis (200–300 °C) and sometimes pyrolysis (over 500 °C) levels (Misnikov 2014).

Mechanical dispersion has a mainly positive effect when applied in the proposed methods of hydrophobic modification. However, dispersion will inevitably reduce the porosity of the peat matrix and, consequently, its sorption capacity. Therefore, it is necessary to perform an experimental assessment of the mass fraction of the ingredients that are supposed to be introduced into the peat, taking into account their individual properties as well as the properties of the composite HMA (moisture, flowability, density, appearance, etc.).

In earlier experiments (Misnikov 2016, 2018), peat particles were ground to a size of less than 100 μm. Direct examination of particle surfaces detected open pores, chips and other defects which can ensure the rapid absorption of liquid water-repellent agents. A detailed analysis of a peat particle fragment using a scanning electron microscope at relatively high magnifications ($\times$3000–6000; Misnikov 2016) shows a branched porous space that provides possibilities for the sorption of water repellents, both in solution (in water or organic solvent) and in their 'pure' forms.

Thus, even at a high degree of grinding, the sorption capacity of peat organic matter will be sufficient for absorption, binding and retention of traditional hydrophobic compounds (active components), both inside and on the surfaces of the particles, at a wide range of concentrations. For example, when oleic acid and ethylhydrosiloxane (NGL-94; see below) are introduced into a matrix of bog and fen peat with moderate decomposition ($R_P = 30$ %; expressed as degree of biochemical decay, see Misnikov 2018) it is possible to achieve mass concentrations up to 20 % without loss of HMA flowability. If higher concentrations of the active component are technologically justified, it is possible to change the base raw material, e.g. to bog peat with a low degree of decomposition ($R_P = 5$–15 %), which is more porous and has a higher sorption capacity.

The investigations described in this article continue the research of Misnikov (2016, 2018) towards developing industrially adapted hydrophobisation methods for cement-based construction materials. The possibility of utilising composite HMAs based on peat and traditional water repellents is examined by means of a generalised analysis of their effect on the physical and mechanical properties of Portland cement.

METHODS

Preparation of complex hydrophobically-modifying additives

The following hydrophobically-modifying additives (HMAs) were trialled:

- HMA-0: dispersed and thermally modified cottongrass-sphagnum bog peat with degree of decomposition $R_P = 45$ % (Misnikov 2016, 2018);

- HMA-10 (Si): HMA-0 (90 %) with ethylhydro-siloxane (10 %);

- HMA-15 (Si): HMA-0 (85 %) with ethylhydro-siloxane (15 %);

- HMA-20 (OA): HMA-0 (80 %) with oleic acid (20 %).

Ethylhydrosiloxane is an organosilicon liquid belonging to the class polyorganohydridesiloxanes, which are organosilicon polymers that contain active

Si-H bonds and Si-O-Si bonds in the main chain. It is industrially manufactured in the Russian Federation as NGL-94 in accordance with the formula $[C_2H_5SiHO]_n$, where n = 10–15). The content of active hydrogen is 1.3–1.45 % of the total mass (Pashchenko 1987). Oleic acid ($C_{18}H_{34}O$) is a monounsaturated fatty acid belonging to the group 'omega-9 unsaturated fatty acids' (Marcos *at al.* 2017), which occurs widely in nature and is found in many vegetable oils (e.g. olive, palm and sunflower oils) as well as in animal fats. The experimental batches of Portland cement were made from clinker and gypsum stone (gypsum dihydrate $CaSO_4 \cdot 2H_2O$) produced at the "Oskolcement" CJSC enterprise, which is part of the international industrial holding "EUROCEMENT Group" (Stary Oskol, Belgorod region).

After preliminary crushing in a jaw crusher to a particle size of less than 5 mm, the clinker and gypsum stone were weighed on an electronic balance, with an error margin of less than 0.1 g, and loaded into a ball mill. The HMAs were also weighed on an electronic balance, with an error margin of less than 0.01 g, and loaded into the mill at the dosages indicated in Table 1. Then, grinding bodies (balls) of total weight of 20 kg were loaded into the mill (in the ratio 1 : 4 (material : grinding bodies)). The method adopted for introducing additives and joint grinding of cement components corresponded exactly with the procedure that is used for industrial production.

The materials were ground until a specific surface area of 320–340 m² kg⁻¹ was obtained, as the reference cement composition (Composition 1 in Table 1). All subsequent cement compositions (with additives) were ground for the same time (1 hour 50

minutes), i.e. for the time required for the reference cement to reach the target specific surface area.

Properties of the cements
The first stage of the research determined the fineness of the obtained cements, their true density, specific surface area and the degree of hydrophobicity. Each cement sample was passed through a sieve with a mesh of 0.9 mm (to separate out fractions larger than 0.9 mm) then mixed until the particle distribution was homogeneous. The grinding fineness of the cement samples was then determined by assessing the residue remaining on a sieve with a mesh of 0.08 mm using a mechanical sieving device. Control sieving was performed manually over a sheet of paper for one minute, and the sieving operation was considered complete if less than 0.01 g of the original cement mass passed through the sieve.

The true density of the cement was determined using the Le Chatelier apparatus. Sixty-five grams of the test cement was loaded into the device in small uniform portions and made up to the zero mark with dehydrated kerosene. After removing air bubbles, the liquid level was determined within the upper graduated part of the device. The true density of the cement ρ_c (g cm⁻³) was calculated by the formula:

$$\rho_c = \frac{m_c}{V} \tag{1}$$

where m_c (g) is the weight of sample cement and V (cm³) is the volume of kerosene displaced by cement. The density of the cement was taken as the arithmetic mean of the results of two parallel determinations, rounded up to 0.01 g cm⁻³.

Table 1. Compositions of the obtained cements.

Composition Number	Materials				
	clinker, g (95 %)	gypsum stone, g (5 %)	additive	additive content	
				%	g
1	4750	250	-	-	-
2	4750	250	HMA-0	3.0	150
3	4750	250	HMA-0	2.0	100
4	4750	250	HMA-0	1.0	50
5	4750	250	HMA-10 (Si)	0.3	15
6	4750	250	HMA-15 (Si)	0.3	15
7	4750	250	HMA-20 (OA)	0.2	10
8	4750	250	HMA-20 (OA)	0.3	15

3

The PSKh-11(MSP) device was used to determine specific surface area and average particle size of the obtained cement samples. The operation of this device is based on the Kozeny-Carman gas permeability method (Vasilevsky *et al.* 2015), and it measures the transit time of a fixed volume of air through a sample layer of cement. The specific surface area was determined as the arithmetic mean of three measurements.

The hydrophobicity of the powder was assessed in terms of the retention time of water drops on the cement surface (Khigerovich & Baier 1979). A sample of the cement under test was placed in a Petri dish in an even layer. The cement was compacted and smoothed with a glass plate over half of its surface area, while the other half remained loose. Five drops of water were applied to each half of the surface and their retention time was recorded.

Properties of cement mortars

The next series of experiments aimed to assess the effect of hydrophobic modifying additives on the physical and mechanical characteristics of cement mortars (cement paste). An AUTOMIX 65-L006/AM mixer with a dosing device for sand was used to prepare the cement mortars. The rotation speeds of the stirring blade were 140 and 285 rpm, and the ratio by weight of sand to cement in the solutions was 3:1. After preparing the solutions, the normal density (N_d) and the timing of the beginning and end of setting (the initial period of strength formation) were determined. Tests for the bending and compressive strengths of samples were carried out on blocks (sample-beams) made from cement-sand mortar, dimensions $40 \times 40 \times 160$ mm, at the ages of 2, 7, 28 and 56 days. Average strength values were determined from measurements on five replicate samples.

The bending strength R_b (MPa) of a single sample-beam was calculated using the formula:

$$R_b = \frac{1.5\ F\ l}{b^3} \qquad [2]$$

where F (N) is the failure load, l (mm) is the distance between support axes and b (mm) is the length of a side of the square section of the sample-beam. The average rate of increase in load on the test sample was 50 ± 10 N s^{-1}.

When determining bending strength, the sample-beam was broken into two approximately equal halves. The sample halves remaining after these experiments were immediately tested for uniaxial compression. In this case, the half of the sample-beam was placed between the pressure plates in such

a way that its edges (horizontal during manufacture) were vertically orientated. The average rate of increase in load on the sample during compression was maintained within 2400 ± 200 N s^{-1}. The compressive strength of a separate half of the sample R_{compr} (MPa) was calculated by the formula:

$$R_{compr} = \frac{F}{S} \qquad [3]$$

where F (N) is the failure load and S (mm^2) is the working surface area of the pressure plate.

Effect of air entrainment

In order to assess the effect of entrained air on the strength of the hardening system, a number of experiments were carried out to determine the average (initial) and additional porosity of the samples. The average density of the cement-sand mortar was determined on samples dried to constant weight at a temperature of 105 °C. Porosity P (%) of the samples was determined using the formula

$$P = \left(1 - \frac{\rho_{av}}{\rho_{tr}}\right) \cdot 100 \qquad [4]$$

where ρ_{av} and ρ_{tr} (kg m^{-3}) are the average and true densities, respectively. The true density of the composition was 2620 kg m^{-3}. Additional porosity ΔP (%) was determined relative to the reference composition by the formula:

$$\Delta P = \frac{\rho_{av\ r} - \rho_{av\ ad}}{\rho_{tr}} \cdot 100 \qquad [5]$$

where $\rho_{av\ r}$ and $\rho_{av\ ad}$ are the average density of the reference composition and the average density of the composition with the additive (kg m^{-3}). This was followed by an analysis of the dependency of relative strength R_{rel} (%) on the additional porosity of the samples.

$$R_{rel} = (R_{max} / R_i) = f(\Delta P) \qquad [6]$$

where R_{max} (MPa) is the maximum strength of the control sample and R_i (MPa) is the strength of the experimental sample.

Influence of the peat component

To assess the effect of the peat component in composite hydrophobic modifiers, a set of experiments was carried out with the additive HMA-0 in low concentrations (0.1 % and 0.3 %), introduced during clinker grinding.

Suppression of air entrainment

To reduce the effect of air entrainment on the quality of the cement mortars, further experiments were carried out using measures to eliminate (or minimise) this negative effect. In the first set of experiments, the cement mortar was stirred manually without using any antifoam additives. In the second set of experiments, antifoam additives (trade marks "Agitan 230" and "Defloam") were added to the cement mortar and the solution was mixed with an automatic mixer (AUTOMIX 65-L006 / AM). The antifoaming agents were added to the solution at a concentration of 0.3 % of the binder weight.

RESULTS

Properties of the cements

Table 2 presents a summary of the measurements of (dry) cement properties. A hydrophobic effect is achieved in cements amended with all of the composite additives trialled (Compositions 5–8).

When using the HMA-0 additive, a stable hydrophobic effect appears only at concentrations of two or more percent (compare Compositions 3 and 4 with Composition 2). Moreover, the use of additives in the tested concentrations does not affect the basic physical and mechanical characteristics of the cements, which comply with the standards of the Russian Federation (GOST 31108-2003, GOST 10178-85) and the European standard EN 197-1.

Properties of cement mortars

The experimental results for the cement mortars (Table 3) show that all of the HMAs tested increase the time to start and end of setting, as well as normal density, which is consistent with previously obtained data (Misnikov 2014). In accordance with the requirements of GOST 10178-85, cement setting should begin no earlier than 45 minutes, and end no later than 10 hours, after starting to mix the solution. The other standards (GOST 31108-2003, EN 197-1) stipulate only the time to start of setting (minimum 60 minutes), and do not regulate the end of setting at

Table 2. Summary of test results for the experimental cements. Here and subsequently, the Composition Numbers correspond to those in Table 1.

Composition Number	Residue in 0.08 mm sieve (%)	Grinding fineness (%)	True density (kg m^{-3})	Specific surface area (m^2 kg^{-1})	Average particle size (µm)	Drop retention time on the surface (min)	
						smooth	loose
1	1.91	98.1	3160	335	5.85	0	0
2	1.56	98.4	3070	352	5.72	> 20.0	> 15.0
3	1.84	99.2	3100	351	5.51	> 5.0	> 5.0
4	2.36	97.6	3120	336	5.81	< 0.5	< 0.5
5	1.95	98.0	3130	336	5.87	> 5.0	> 5.0
6	1.93	98.1	3130	341	5.77	> 20.0	> 15.0
7	1.91	98.1	3140	335	5.79	> 15.0	> 15.0
8	1.93	98.1	3130	341	5.81	> 20.0	> 20.0

Table 3. Characteristics of the experimental cement mortars. Composition Numbers as in Table 1.

Composition Number	Normal density (%)	Time of setting (min)		Strength (MPa)							
		beginning	end	2 days		7 days		28 days		56 days	
				R_b	R_{compr}	R_b	R_{compr}	R_{br}	R_{compr}	R_b	R_{compr}
1	26.8	200	225	5.8	21.9	8.6	38.3	9.9	51.3	10.4	57.5
2	32.5	1140	1200	3.6	13.8	5.1	16.9	6.2	25.6	6.6	27.6
3	31.0	780	885	4.1	14.2	6.0	23.9	7.2	29.8	7.9	34.3
4	31.0	360	405	4.5	14.8	6.7	30.7	8.5	39.4	8.9	43.8
5	28.0	480	615	3.9	9.7	6.1	18.5	7.1	25.5	6.7	25.8
6	27.8	505	855	3.8	10.1	5.7	17.9	6.8	23.5	6.4	23.9
7	27.2	485	790	3.6	7.9	5.6	15.9	6.2	19.5	6.9	28.5
8	27.7	495	835	3.4	6.9	5.1	12.3	5.9	17.6	6.5	24.2

all. Thus, all investigated compositions meet the requirements of GOST 31108-2003 and EN 197-1 in terms of beginning and end of setting.

It should be noted that all of the HMAs tested have a negative effect on the kinetics of strength gain, as well as on the strength of the cement samples themselves. This is hypothetically due to the process of mixing cement and cement mortar with water which, over a certain period of time, might lead to entrainment of additional air into the system under test. Moreover, it is known (Ozersky *et al*. 2021) that the air-entraining effect is enhanced when using various types of organic (including bitumen-containing) additives (Misnikov 2016).

Effect of air entrainment
The results indicated an increase in porosity and, accordingly, additional porosity in hydrophobically-modified cements (Table 4). The quantitative indicators increase with increasing concentrations of additives. At the same time, additives enriched with traditional hydrophobic components have the greatest effect on the qualitative increment of additional porosity in the samples.

It is necessary to pay attention to the amount of additional porosity achieved when using various additives. For example, the introduction of thermally activated peat (HMA additive) at dosages ranging from 1 % to 3 % during clinker grinding increases the additional porosity of the cement stone from 4.6 % to 8.7 %. At the same time, the introduction of composite hydrophobic modifiers in much lower concentrations (0.2–0.3 %) increases the porosity much more, from 11.4 % to 13.6 %. This indicates that, in terms of the active substance, the air-entraining effect of traditional modifying compositions is two orders of magnitude greater than the effect of a peat hydrophobisator.

Analysis of the relationship $R_{rel} = f (\Delta P)$ (Equation 6, Figure 1) makes it possible to fully confirm the negative influence of porosity on the strength of cement. The dependence of strength on additional porosity is exponential, with correlation coefficients close to unity.

Table 4. Effect of additional porosity on sample strength, determined at age 28 days. Composition Numbers as in Table 1.

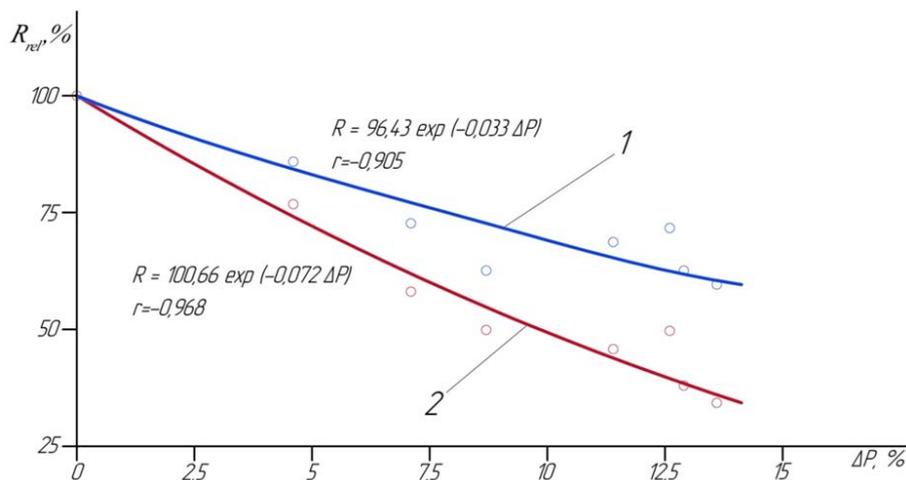| Composition Number	Average density (kg m^{-3})	Porosity P (%)	Additional porosity ΔP (%)	Relative strength R_{rel} (%)	
				bending	compression
1	2135	18.5	0	100	100
2	1906	27.3	8.7	62.6	49.9
3	1948	25.6	7.1	72.7	58.1
4	2013	23.2	4.6	85.9	76.8
5	1805	31.1	12.6	71.7	49.7
6	1835	30.0	11.4	68.7	45.8
7	1798	31.3	12.9	62.6	38.0
8	1779	32.1	13.6	59.6	34.3

Figure 1. Dependence of the relative strength R_{rel} (%) of cement mortar on additional porosity ΔP (%), for (1) bending and (2) compression.

Influence of the peat component

The experiments established that, at low concentrations of peat additives (HMA-0), the qualitative characteristics of cement hardly change and comply fully with current Russian and European regulations (EN 197-1, GOST 31108-2003, GOST 10178-85; Table 5). However, such concentrations are clearly insufficient to achieve a hydrophobic effect in a mineral binder.

Suppression of air entrainment

The results (Table 6) showed that even the simple application of manual stirring of the solution can reduce the additional porosity by 3.7–4.4 times. Moreover, this effect is manifested better with the HMA-0 additives than with the compositional modifier (HMA-20). The use of defoamers reduces the negative effect of air entrainment by 5.5–11.3 times. It is characteristic that defoamers have the greatest effect on traditional water repellents (in our case, on oleic acid).

DISCUSSION

The negative effect of porosity on the strength of cement mortars, concretes and building structures based on them is quite logical and unquestionable. However, a number of established studies (Alentyev *et al.* 1962, Pashchenko 1987) on hydrophobisation methods for cements do not demonstrate a negative effect on strength characteristics. Therefore, a retrospective analysis of scientific papers on the subject has been carried out to clarify the possible reasons for this inconsistency.

Large-scale fundamental studies on the influence of various organosilicon compounds (including ethylhydrosiloxane), oil refining waste and materials of biological origin (e.g. oleic acid) on the hydrophobicity of building materials were carried out in the second half of the 20th century (Khigerovich 1957, Vanderbilt & Simko 1960, Alentyev *at al.* 1962, Vanderbilt & Jaruzelski 1962, Sterman & Marsden 1963, Erickson *et al.* 1964, Khigerovich &

Table 5. Test results for the properties of Portland cement with peat (HMA-0) additive at two concentrations.

№	Indicator	Type of Portland cement		
		control	with 0.1 % HMA-0	with 0.3 % HMA-0
1	Specific surface area ($m^2 kg^{-1}$)	352	360	349
2	Normal density of cement paste (%)	24.5	26.0	26.0
3	Water : cement ratio	0.37 : 1	0.37 : 1	0.37 : 1
4	Beginning of setting (min)	145	195	195
5	End of setting (min)	205	255	270
6	Bending strength limit at 3 days (MPa)	5.7	6.1	6.0
7	Compressive strength limit at 3 days (MPa)	36.8	35.9	35.2
8	Bending strength limit at 28 days (MPa)	6.6	6.4	6.2
9	Compressive strength limit at 28 days (MPa)	47.7	45.5	44.8

Table 6. Dependence of the strength of cements on the additional porosity of the compositions when measures for suppressing air entrainment were incorporated. Composition Numbers as in Table 1 with suffixes (where appropriate) D: "Defloam" additive used; A: "Agitan" additive used; M: manual stirring.

Composition Number	Additional Porosity ΔP (%)	Bending (R_b) and compressive (R_{compr}) strength							
		2 days				28 days			
		R_b		R_{compr}		R_b		R_{compr}	
		MPa	%	MPa	%	MPa	%	MPa	%
1	0	5.8	100	21.9	100	9.9	100	51.3	100
3	7.1	0	0	0	0	7.2	72.7	29.8	58.1
3 D	1.3	4.1	70.7	13.3	60.7	9.3	93.9	53.6	104.5
3 M	1.6	2.9	50.0	8.3	37.9	8.1	81.8	45.7	89.1
8	13.6	3.4	58.6	6.9	31.5	5.9	59.6	17.6	34.3
8 A	2.0	4.7	81.0	16.3	74.4	9.3	93.9	49.0	95.5
8 D	1.2	4.7	81.0	16.3	74.4	9.4	94.9	49.0	95.5
8 M	3.7	4.4	75.8	15.9	72.6	8.1	81.8	39.5	77.0

Baier 1979, Pashchenko 1987). The results are now widely used in various industries. As a rule, new data appearing in modern literature complement and clarify these fundamental studies. They mainly consider specific cases, from science and production industry, of the effects of water repellents on various materials including hydrophobic powders (He *et al.* 2015), mortar surface (Novak & Zach 2018, Barnat-Hunek *et al.* 2020), clay brick and mortar (Barnat-Hunek & Smarzewski 2015, Soulios *et al.* 2020), cement mortars (Lagazzo *et al.* 2015, Grabowska & Koniorczyk 2019), concrete mortars and concretes for special purposes (Babiak *et al.* 2018, Al-Kheetan *et al.* 2019, Al-Kheetan *et al.* 2020), concrete fillers (Suchorab *et al.* 2016), and thermal insulation materials (Kumar *et al.* 2016). A separate relevant field of study deals with the development of superhydrophobic surfaces and coatings (Muzenski *et al.* 2015, Li *et al.* 2016, Makaryan *et al.* 2016, Cao *at al.* 2020a, Cao *at al.* 2020b, Chen *et al.* 2020, Zhu & Liao 2020). Particular importance is attached to the use of natural and biogenic materials in these technologies (Ghasemlou *et al.* 2019, Saji 2020).

Analysis of these literature sources along with the results of the present study, in terms of the effect of traditional water repellents on the strength of cement, indicates a number of contradictions. For example, Alentyev *at al.* (1962) and Pashchenko (1987) researched the effect of ethyl hydrosiloxane fluid on the strength of cement. Water repellent in a 'pure' form was introduced during the grinding of clinker (as in the current study) in concentrations of 0.04, 0.08 and 0.15 %. An increase in the compression strength of samples with a sand : cement ratio of 3:1 and a water : cement ratio of 0.45 : 1 was observed in all experiments (Table 7).

Earlier work, in which oleic acid was used as a water repellent (Khigerovich 1957, Khigerovich & Baier 1979), showed more modest results. The activity of freshly prepared cements, determined by compressive strength tests, increased by 5–13 % compared to the control sample in a number of

experiments, and decreased by 5–10 % in some, so on average it hardly changed (Table 8). However, a slowdown in strength gain was noted in hydrophobic cements during the early stages of hardening. Similar fluctuations in strength were observed in all other experiments on cements made using various types of clinker and high-performance grinding equipment. However, when the tests were repeated after 1.5–2 months, the strength of the hydrophobic cements was significantly higher in all cases because the control cements had lost activity during storage. The work of Griffin & Lorman (1957), carried out at the request of the US Navy, also showed that cement hydrophobised with oleic acid was resistant to hydration during storage. But at the same time, the strength of concrete (or mortar) made with such cement decreased significantly. This was explained (as in the present case) by the air-entraining effect of oleic acid. Moreover, the use of tri-n-butyl phosphate $(C_{12}H_{27}O_4P/(C_4H_9)_3PO_4)$, as a contemporary air-suppressing additive, did not provide the required effect - it was not possible to reduce the excess strength drop (Stoll 1958). The use of this chemical compound suffers from the additional disadvantage that it is a toxic substance and carcinogenic. In one of the more recent studies (Albayrak *et al.* 2005), the negative effect of oleic acid on concrete strength was also confirmed (a decrease of about 50 %).

Table 7. Calculated relative strength of cement when using ethylhydrosiloxane fluid NGL-94, according to Alentyev *et al.* (1962) and Pashchenko (1987).

Age of samples	Relative compressive strength (%)			
	control cement	cement with additive %		
		0.04	0.08	0.15
3 days	100	108	128	192
7 days	100	111	123	168
28 days	100	110	114	130

Table 8. Changes in the properties of cement during hydrophobisation with oleic acid at a concentration of 0.1 % (Khigerovich 1957).

Clinker type	Cement type	Normal density (%)	Compressive strength (MPa) at age		
			3 days	7 days	28 days
Belite	control	24.5	38.6	50.0	52.4
	hydrophobic	30.0	38.1	49.5	55.4
Silica	control	24.5	26.6	37.3	46.7
	hydrophobic	29.0	23.8	36.3	50.5
Aluminous	control	25.5	34.6	36.1	48.5
	hydrophobic	30.0	38.8	34.1	43.4

The work of Alentyev *at al.* (1962) and Pashchenko (1987) recorded the greatest increase in strength at early hardening times and at the highest concentration of the hydrophobic agent, in contradiction to the data obtained in the present study (Table 4). For example, in Compositions 5 and 6 the concentration of the active ingredient (ethylhydrosiloxane liquid) is 0.03 % and 0.045 %, respectively (Table 1). Even at such low concentrations there is a steady decline in strength at all stages of hardening (Table 3), and it is to be expected that strength will decrease with increasing amount of a hydrophobic agent. Also, Compositions 7 and 8 (Table 1) contain, respectively, 0.04 % and 0.06 % of the active substance (oleic acid), which corresponds approximately to the concentration used by Khigerovich (1957). However, in the present case, there is a significant loss of strength (Table 3).

The results of the experiments with low concentrations of peat (HMA-0) additives (Table 5) establish that the loss of strength and change in other quality indicators of cements when using composite additives is not caused by the peat matrix, but by the action of traditional water repellents.

The differences between the results of studies in 1950–1980 and the present data can be explained by differences in the methods of preparation of cement mortars for testing. In the 1950–1980 studies there was no critical entrainment of air into the system because, as a rule, the components used for the preparation of cement mortars were mixed manually at that time. Nowadays, laboratories usually utilise high-speed automatic mixers. It should be noted that the mixers used in industry have a physical and mechanical effect on the solution which is typical for manual(!) mixing.

As expected, the use of methods for suppressing air entrainment during the preparation of cement mortars reduces the increment of porosity and, accordingly, increases the strength. For example, referring to Table 6, the combinations that include HMA-0 and apply simple manual stirring of the solution demonstrate an increase in the relative compressive strength at 28 days from 58.1 % to 89.1 %. In the solutions with added HMA-20 (OA), the effect of using manual stirring is also quite high; the strength increased from 34 % to 77 %. At the same time, standard air suppression methods (using additives "Agitan 230" and "Defloam") showed even greater efficiency, completely removing the negative effect of hydrophobic modifiers on strength. In these experiments, strength increased from 95.5 % to 104.5 % compared to the control sample, providing a basis for obtaining high-quality hydrophobically modified cements that meet the requirements of the current regulatory documents.

Thus, some main directions have been identified for improving the quality characteristics of HMAs, as well as approaches to achieving effective HMA compositions that meet modern regulatory requirements. These directions include:

1. the preparation of compositions in which modified peat is used as a matrix for the accumulation and retention of water repellents that are already used in the cement industry;

2. the additional use of additives that suppress entrainment of air into the hardening cement mortar; and

3. the use of techniques for preparation of cement mortars which exclude (or minimise) the entrainment of air into the hardening cement mortar.

Since the regulatory documents limit the content of organic additives in mineral binders to 0.3–0.5 %, further research is needed to form an evidence base for the safety of increasing their concentration.

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